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NUCLEAR SPIN ECHOES AND MOLECULAR SELF-DIFFUSION IN LIQUIDS

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ABSTRACT. The nuclear spin-echo phenomenon and the effect of molecular self-diffusion in liquids on the spin-echoes have been treated on the basis of a new stochastic model The physical and mathematical inconsistencies of similar treatments reported earlier have also been discussed A spin-echo method for measuring the co-efficient of molecular self-diffusion D directly, using the "image echo" has been developed, which completely eliminates the relaxation damping of the echo signal. It has also been shown that the diffusion damping co-efficient k thus determined can be utilized for an independent measurement of transverse relaxation time T_2 even in presence of appreciable diffusion These methods have been used in the case of water, and the values of D and T_2 obtained agree well with other measurements. Further, a direct experimental check has been furnished to compare the validity of different theoretical approaches to this problem

1 INTRODUCTION

The mechanism of formation of nuclear spin-echoes and the effect of molecular self-diffusion on the echo-amplitudes have been discussed previously by various authors [Hahn (1950), Das and Saha (1954), Carr and Purcell (1954), Herzog and Hahn (1956), Torrey (1956) and Douglass and McCall (1958)]. The equilibrium (thermal) magnetization of a substance when placed in a steady magnetic field, is deflected from the direction of the magnetic field by a short radio frequency (rf) pulse and during the absence of the pulse the nuclear magnets execute Larmor precession (Lp) about the steady field with different Larmor frequencies (Lf) because of inhomogeneity in the magnetic field After a certain time-interval τ, if a second short rf pulse is used to reverse the phase accumulated by the nuclear magnets, the nuclei will recluster completely at the end of the next interval τ and give the echo signal This complete reclustering will be possible only when the phase accumulations of individual groups are equal in the two intervals. If, however, there be any process that makes these phase accumulations unequal, the reclustering at the end of the interval 2τ will not be complete and the echo amplitude will diminish. The diminution will depend on τ if the phase accumu-

* One should note that the random motion of the molecules will also average out the "local field" and give rise to relaxation damping of the nuclear induction signals. T_1 and T_2 in Bloch equations (1) take account of this effect.

lation due to that process is time dependent. The random (Brownian) motion of the molecules in a liquid is such a process*. This process carries the molecules along with the resonating nuclei to different sites in the inhomogeneous magnetic field, thereby changing their *Lf* and hence the phase of their *Lp*. Since this is a Markoffian process, the phase-accumulations will not be proportional to first power of time, and as a result they will not be equal in the two intervals. Thus, there will be damping of the echo-amplitude which has been called the diffusion damping by Hahn. If instead of two pulses, three pulses are used to form the echoes the above effect of molecular self-diffusion will manifest itself in the different echoes in different ways. This effect has been discussed by Hahn and later corrected by Herzog and Hahn and by Das and Saha in the three-pulse echo system. Their methods have been examined in some details at the end of Section II.

The present work considers the following model. The random molecular motion is described by the motion of any representative molecule with proper initial distribution in Larmor frequencies (conforming with the actual physical situation). Such a distribution can be represented by Dirac's δ-function as in the case of liquid molecules executing Brownian motion [Green (1952)]. The whole time-interval in which we are interested is divided into a large number of small sub-intervals, and the damping of the echo signal due to random phase-accumulations in the successive short intervals, that arise through random change in Larmor frequency has been taken into account through the change in Larmor frequency which follows a Markoff process* [Chandrashekhar (1943), Wang and Uhlenbeck (1945), Anderson (1954), Herzog and Hahn (1956)], satisfying Chapman-Kolmogoroff equation. The results of such calculation agree with those from the straightforward treatments of Carr and Purcell and of Torrey when extended to echoes for Carr-Purcell pulse sequence.

On the basis of this formulation, experimental methods for the determination of self-diffusion constant, D, and the transverse relaxation time T_2, have been developed. In these methods the diffusion-damping co-efficient k ($= \gamma^2 G^2 D$, where γ, G and D have the usual meaning) can be obtained without previous determination of T_2. This value of k is then used to obtain T_2 from Carr-Purcell method in general cases, which has been described in details in Section IV. Besides obtaining a satisfactory value for D and T_2, an independent experimental check of the physical basis of the theoretical formulation has also been described.

In Section II, the theoretical formulation is presented with criticism of Das and Saha's and of Herzog and Hahn's treatments. In Section III, the apparatus used is briefly described. The Section IV contains the experimental methods for

* A collection of the relevant papers on Markoff Process can be found in "Noise and Stochastic Processes", edited by N. Wax., Dover Publications, New York, (1954).

measurement of D and T_2, and the results. In the last Section V, the different experimental methods for measuring D and T_2 have been critically examined.

II THEORETICAL FORMULATION

Let us start with the Bloch equations (Bloch, 1946) which have been proved satisfactory in describing the dynamical behaviour of nuclear magnetization. The equations can be written in a co-ordinate system rotating with the pulsed-*rf* frequency, ω as [Bloch, 1946, Rabi *et al*, 1954]

$$\frac{du}{dt}+\eta v=-\frac{u}{T_2}$$

$$\frac{dv}{dt}=-\eta u+Rw-\frac{v}{T_2}$$

and

$$\frac{dw}{dt}=Rv-\frac{w-w_0}{T_1} \quad . \quad (1)$$

Here u, v, w, w_0 and η have a slightly different meaning than the usual. The molecules carrying the nuclear magnets execute random (Browman) motion in an externally applied inhomogeneous magnetic field. To take account of the effect of this random motion on the spin-echo phenomenon, the Bloch equations have been assumed to be true for the average magnetization of a molecule at a point (x, y, z) inside the sample u, v and w are the x', y' and z' components, respectively of the average molecular magnetization $\boldsymbol{M}_{mol}$. w_0 is the equilibrium value of magnetization at thermal equilibrium and is given by $w_0=\chi_{mol}\,H_z\,(x,\ y,\ z)$, χ_{mol} being the static molecular susceptibility, $R=\gamma H_1$ and $\eta=\gamma H_z\,(x, y, z)-\omega$; H_1 is the half amplitude of the applied linearly polarised *rf* field, $2H_1\cos\omega t$

One of the two circularly polarized components of the *rf* field is actually effective in producing resonance. $H_z\,(x, y, z)$ is the value of the externally applied magnetic field at the point (x, y, z). T_1 and T_2 are the usual longitudinal and transverse relaxation times respectively as introduced by Bloch. The random change of position of the molecule causes a corresponding change in the value of η. This random motion is of the nature of the stationary Markoff process. On the average this motion is well represented by the Langevin equation (Kirkwood, 1946 & Green, 1952).

In order to find out the magnetization under study at any subsequent time from its initial value we have to follow the motion of such a molecule In following the motion of the molecule we shall have to keep in mind that the magnetization must satisfy the Bloch equations whereas its position co-ordinates and hence η will be obtaind from the Langevin equation. For the solution of the

Bloch equations under such conditions we divide the whole time interval from the start of the pulse sequence into a large number of small sub-intervals. These sub-intervals are of such magnitude that the root mean square change in η is very small Under such conditions we can solve the Bloch equations during these sub-intervals taking η to be constant; the stochastic nature of η is taken into account through the inclusion of a transition probability corresponding to the change in η from its initial value at the beginning of the sub-interval to the final value at the end of the sub-interval. The integration over the initial value of η for the interval will give us the value of magnetization at the time we are interested in, and it is a function of η corresponding to that time.

Analytically, let $\Phi(\eta_s, t_s)$ be the solution of the Bloch equations for a certain value of $\eta(=\eta_s)$. Since η is a stochastic variable, the value of magnetization with a certain value of $\eta(=\eta_s)$ must be expressed as

$$F[\eta_s, t_s] = \Phi(\eta_s, t_s)W(\eta_s, t_s)$$

where $W(\eta_s, t_s)$ expresses the probability that at time t_s we have the value of η as η_s. As η follows a Markoff process $F[\eta_s, t_s]$ can be related with its value at any other time by a relation like the Chapman-Kolmogoroff equation:

$$F[\eta_s, t_s] = \int_{-\infty}^{\infty} F[\eta_i, t_i]\, T(\eta_s, t_s \mid \eta_i, t_i)\, d\eta_i$$

Here $T(\eta_s, t_s/\eta_i, t_i)$ denotes the transition probability of the change of η_i to η_s in time $t_s - t_i$. This transition probability, in general, will be product of two transition probabilities, namely $B(\eta_s, t_s/\eta_i, t_i)$ and $P(\eta_s, t_s/\eta_i, t_i)$. The first one is obtainable from the solution of Bloch equations if we could treat η also to be varying during the period. The second one can be obtained from the solution of Langevin equation. Now, if the time-interval $t_s - t_i$ is considered to be very small such that the change in η during the interval is small, but is of sufficient magnitude such that the force causing the displacements of the particles and hence the change of η fluctuates a large number of times, we have

$$B(\eta_s, t_s \mid \eta_i, t_i) \simeq B(\eta_i, t_s \mid \eta_i, t_i)$$

and $$P(\eta_s, t_s \mid \eta_i, t_i) \simeq \left\{ \frac{1}{4\pi k(t_s - t_i)} \right\}^{\frac{1}{2}} \exp \left\{ -\frac{(\eta_s - \eta_i)^2}{4k(t_s - t_i)} \right\}$$

(see expression (6))

with these assumptions,

$$F[\eta_s, t_s] = \int_{-\infty}^{\infty} \Phi(\eta_i, t_i)B(\eta_i, t_s \mid \eta_i, t_i)\, W(\eta_i, t_i)\, P(\eta_s, t_s \mid \eta_i, t_i) d\eta_i$$

$$= \int^{\infty} \Phi(\eta_i, t_s)W(\eta_i, t_i)\, P(\eta_s, t_s \mid \eta_i, t_i) d\eta_i$$

This relation shows that if we know the initial value of F, we can deduce its value at any other time

Let us now consider a particle situated initially at the point (x_0, y_0, z_0). The magnetization at $t = 0$ can be represented by

$$u[0, \eta] = u(0)W(\eta, 0) = 0$$

$$v[0, \eta] = v(0)W(\eta, 0) = 0$$

and
$$w[0, \eta] = w(0)W(\eta, 0) = w_0\delta(\eta - \eta_0) \quad .. \quad (2)$$

The initial distribution has been taken in the form of Dirac δ-function as the position of the particle is definite at the point (x_0, y_0, z_0), and hence $\eta_0 = \gamma H_z (x_0, y_0, z_0) - \omega$. For the most general field distribution

$$H_z(x_0, y_0, z_0) = H_z(0) + x_0 \left(\frac{dH_z}{dx}\right)_0 + y_0 \left(\frac{dH_z}{dy}\right)_0 + z_0 \left(\frac{dH_z}{dz}\right)_0 + ..$$

terms with higher derivatives of H_z. $H_z(0)$ is the value of the steady magnetic field at the origin. For simplicity the field gradient can be taken to be constant and unidirectional (in the direction of z), and η_0 can be written as

$$\eta_0 = \gamma H_z(0) - \omega + \gamma G z_0 \quad .. \quad (3)$$

where $G = \frac{dH_z}{dz}$. At exact resonance $\gamma H_z(0) - \omega = 0$. The treatment, which has been followed here for this simple case, can be easily shown to be valid for multi-directional field gradients as well as for off-resonance conditions*.

Hence, considering any time-interval t, we divide it into a large number, say n of small and equal sub-intervals of Δt each, such that $n\Delta t = t$ and assign values to η at the beginning and at the end of each sub-interval. For example, η_{m-1} and η_m are these values for the m-th sub-interval. For the m-th sub-interval the Bloch equations are solved taking η_{m-1} to be constant, and we obtain $\phi(\eta_{m-1},$

* Since the results of this formulation (taking the field gradient in the z-direction as constant, and neglecting the field gradients in other directions) are used to interpret data obtained with a magnet where these conditions are not strictly valid, it is interesting to investigate the effects due to (a) G being not constant, and (b) the gradients in the x and y directions are not zero. It can be easily shown that none of these affects the result appreciably. Both the situations, described above, introduce small error in the value of k, but the time-dependence of the signal amplitudes remains almost unaffected. To test these points experimentally, the time dependence of the amplitude of the image echo was recorded without applying any field gradient in z-direction externally. Even in this case (where the field-gradient is multidirectional) the time dependence was found to be parabolic as the equation (14) predicts.

$m\Delta t)$ where ϕ stands for u, v and w components. $F[\eta_m, m\Delta t]$ is then obtained by using the relation

$$F[\eta_m, m\Delta t] = \int_{-\infty}^{\infty} F[\eta_{m-1}, m\Delta t]\, P(\eta_m, \Delta t \,|\, \eta_{m-1}) d\eta_{m-1} \quad \ldots \quad (4)$$

where $P(\eta_m, \Delta t \,|\, \eta_{m-1})$ is the probability of η_{m-1} changing to η_m in the time-interval Δt. Using the relation

$$\eta_m - \eta_{m-1} = \gamma G(z_m - z_{m-1}) \quad \ldots \quad (5)$$

$P(\eta_m, \Delta t \; \eta_{m-1})$ can be obtained from the solution of Langevin equations, and the expression for it comes out as

$$P(\eta_m, \Delta t \,|\, \eta_{m-1}) = \left(\frac{1}{4\pi k \Delta t} \right)^{\frac{1}{2}} \exp \left\{ - \frac{(\eta_m - \eta_{m-1})^2}{4k\Delta t} \right\} \quad \ldots \quad (6)$$

where $k = \gamma^2 G^2 D$, D being the co-efficient of molecular self-diffusion. The Eq. (1) take different forms in the presence and in the absence of the rf-pulse, and the usual solutions in the two cases are each treated as ϕ as discussed above. The thermal equilibrium value of w-component can be shown to be given by

$$w_0[\eta_n, n\Delta t] = w_0 \int_{-\infty}^{\infty} \delta(\eta - \eta_0)\, P(\eta_n, n\Delta t \,|\, \eta) d\eta = w_0\, P(\eta_n, n\Delta t \,|\, \eta_0) \quad \ldots \quad (7)$$

The final value of $F(t)$ is then obtained from the relation

$$F(t) = \int_{-\infty}^{\infty} F[\eta_n, n\Delta t] d\eta_n \quad \ldots \quad (8)$$

This is the value of magnetization for a single particle We obtain the total magnetization $M(t)$ due to the whole sample by using the relation

$$M(t) = N \iiint F(t) dV \quad \ldots \quad (9)$$

where the integration extends over the whole sample volume and N is the number density of the molecules.

For a cylindrical sample-holder and for the constant field gradient in the z-direction, the volume integral gives an expression of the form

$$\frac{2M_0 J_1(p)}{p} \quad \ldots \quad (10)$$

where for primary echo,

$$p = \gamma G a(t - 2\tau_1) \quad \ldots \quad (11)$$

TABLE I

Expressions for the echoes and the free induction signals for three pulses of nutational angles ξ_1, ξ_2 and ξ_3, applied at times $t = 0$, τ_1 and τ_2 respectively, as obtained by the present treatment.

Position of the signals	Time independent part of the amplitudes at signal maxima	Time dependent part of the amplitudes at the signal maxima: Part dependent on relaxation	Time dependent part of the amplitudes at the signal maxima: Part dependent on molecular self diffusion
0	$-M_0 \sin \xi_1$	1	1
τ_1	$-M \sin \xi_2$	$1+(\cos \xi_1 - 1) \exp\left(-\frac{\tau_1}{T_1}\right)$	1
τ_2	$-M_0 \sin \xi_3$	$1+\left[\left\{1+(\cos \xi_1 - 1) \exp\left(-\frac{\tau_1}{T_1}\right)\right\} \times \cos \xi_2 - 1\right] \exp\left(-\frac{\tau_2-\tau_1}{T_1}\right)$	1
$2\tau_1$	$M_0 \sin \xi_1 \sin^2 (\xi_2/2)$	$\exp\left(-\frac{2\tau_1}{T_2}\right)$	$\left[\exp\left(-\frac{2}{3} k \tau_1^3\right)\right]$
$2\tau_2$	$M_0 \sin \xi_1 \cos^2 (\xi_2/2) \sin^2 (\xi_3/2)$	$\exp\left(-\frac{2\tau_2}{T_2}\right)$	$\left[\exp\left(-\frac{2}{3} k \tau_2^3\right)\right]$
$2(\tau_2-\tau_1)$ (Image echo)	$-M_0 \sin \xi_1 \sin^2 (\xi_2/2) \sin^2 (\xi_3/2)$	$\exp\left[-\frac{2(\tau_2-\tau_1)}{T_2}\right]$	$\left[\exp\left[-\frac{2}{3}\left\{k\tau_1^3+(\tau_2-2\tau_1)^3\right\}\right]\right]$
$[2\tau_2-\tau_1]$	$[M_0 \sin \xi_2 \sin^2 (\xi_3/2)]$	$\left[1+(\cos \xi_1 - 1) \exp\left(-\frac{\tau_1}{T_1}\right)\right] \times \exp\left[-\frac{2(\tau_1-\tau_1)}{T_2}\right]$	$\exp\left[-\frac{2}{3} k(\tau_2-\tau_1)^3\right]$
$\tau_2+\tau_1$	$\frac{1}{2} M_0 \sin \xi_1 \sin \xi_2 \sin \xi_3$	$\exp\left[-\frac{2\tau_1}{T_2}-\frac{\tau_2-\tau_1}{T_1}\right]$	$\exp\left[-k\left\{\frac{2}{3}\tau_1^3+\tau_1^2(\tau_2-\tau_1)\right\}\right]$
$2n\tau$ (Carr-Parcell echoes*)	$(-1)^{n-1}M_0$	$\exp\left[-\frac{2n\tau}{T_2}\right]$	$\exp\left[-\frac{2}{3} kn\tau^3\right]$

* Echoes obtained at time $t=2n$ after the application of a series of n 180° pulses at times $t=(2n-1)$ following a 90° pulse applied at $t=0$.

a is the internal radius of the sample holder, J_1 is the first order Bessel function of the first kind. This represents the shape of the echo and of the free induction signals. For constant field gradients in the three directions, this is given by

$$\frac{2M_0 J_1(p)}{p} \cdot \frac{\sin q}{q} \qquad \ldots \quad (12)$$

where for primary echo,

$$p = \gamma \left\{ \left(\frac{dH_z}{dz}\right)^2 + \left(\frac{dH_z}{dr}\right)^2 \right\}^{\frac{1}{2}} a(t-2\tau_1)$$

and

$$q = \gamma \left(\frac{dH_z}{dy} \right) b(t-2\tau_1) \qquad \ldots \quad (13)$$

b is the effective length of the sample.

Using the above scheme and the usual technique of matching the Bloch equations, the different free induction signals and the different echo signals for any number of pulses of arbitrary nutational angles can be obtained. The results of such calculations for three pulses applied at time $t = 0$, τ_1 and τ_2 are shown in Table I. Table I also contains the expressions for the amplitudes of the echoes occurring at $t = 2n\tau_1$, when a first 90°-pulse followed by a series of n 180°-pulses are applied at times $t = \tau_1, 3\tau_1, \ldots (2n-1)\tau_1$. This expression agrees with that obtained by Carr and Purcell and later by Torrey for such pulse sequences. The expressions for the image echo at maximum amplitude, as obtained by different theoretical approaches, have been shown in Table II. The disagreement observed is expected since some of the earlier methods were not rigorously correct, and we discuss them below.

Herzog and Hahn (1956) have extended their method, used in solids, to the case of liquids. If, however, one uses the Eqns (23) and (25) of their paper to calculate the amplitude of the free precession signals in liquids, one obtains infinite amplitude for the signals*. The reason for this can be seen to be the assumption

$$P(\eta_0) = \text{constant}.$$

Moreover, the above assumption does not represent the physical situation. Also the diffusion-process in liquid can not be described in exactly the same way as

* The equations in the appendix of Herzog and Hahn's paper giving the signal amplitudes in liquids show finite amplitude since the integration was not fully carried out. Actually they should get, for example, $E_{max} \sim \exp[-\frac{2}{3} k\tau^3]\, \delta(o)$, for the primary echo, where $\delta(o)$ is the Dirac's δ-function for the zero value of the parameter i.e. at $t = 2\tau_1$. Similar will be the case with other signals.

TABLE II

Expressions for the amplitude of the image echo at echo maximum, according to different theoretical approaches. θ denotes the time of occurrence of the echo maximum, measured from the third puse i.e., $\theta = \tau_2 - 2\tau_1 = \tau - \tau_2 - \tau_1$ where τ_1 and τ_2 are positions of the second and the third pulses respectively. Echo maximum occurrs at $t = 2(\tau_2 - \tau_1)$ znd ξ_1, ξ_2 and ξ_3 are the nutational angles of the applied pulses as in Table I

		Common part of the echo-amplitude, as given by different theoretical approaches	Part dependent on diffusion
1	Hahn	$-M_0 \sin \xi_1 \sin^2 (\xi_2/2) \sin^2 (\xi_3/2) \times \exp\left[-\frac{2(\tau_2 - \tau_1)}{T_2}\right]$	$\exp\left(-\frac{8}{3} k\tau^3\right)$
2.	Das and Saha	,,	$\exp\left[-k\left\{\frac{5}{3}\tau^3 - 4\tau^2\theta + 5\tau\theta^2 - \theta^3\right\}\right]$
3.	The present treatment*	,,	$\exp\left[-2k\left\{\frac{1}{3}\tau^3 - \tau^2\theta + \tau\theta^2\right\}\right]$

* The same results can be also derived from Torrey's (1956) treatment based on the solution of diffusion equation.

they have done in the case of solid. The stationary distribution as obtained from "the probability distribution for the frequency" (see Eq. (31) of their paper) reduces to zero as $t \to \infty$. Their treatment will be valid in the case of liquid also if the probability distribution for the frequency is taken in such a way that it conforms with the actual stationary distribution in liquids We, however, note that the damping terms in equations for the free precession signals in liquids as given in their paper are identical with ours. This is because the damping terms depend on the probability distribution for the frequency (transition probability) and on the phase factor coming through the solution of the Bloch equations; and these are the same both in our treatment and in Herzog and Hahn's.

The treatment of Das and Saha contains the following important points —

(1) They assigned definite phase (as they termed) and the Larmor frequency change for each of the free precession intervals. In essence it is equivalent to the splitting up of the actual phase accumulated in any free precession interval into two parts :-

(a) the phase accumulated when the Larmor frequency remains constant in the interval considered, and

(b) the difference between the total phase accumulated and the part described in (a).

In averaging these phase accumulations, they have separately averaged over the two parts considering them to be following independently the Gaussian distribution law. The justification for such treatment is yet to be shown.

(2) They separately considered the phase accumulations in the different free precession intervals. This is not justified for the following reasons :

(a) since the accumulated phase does not follow the Markoff process, the averaging of phase in successive free precession intervals comprising the total interval is not justified.

(b) since the echo signals are made possible due to the preservation of the phase-memory by the nuclear magnets, the consideration of the phase accumulations in different free precession intervals as completely independent does not conform with the physical situation.

Since they considered phase averaging in this way, the phase-reversal could not be taken into account in their treatment

III. APPARATUS

The apparatus used has been reported earlier by Banerjee *et al.* in this journal (Banerjee *et al.*, 1957). The addition to the apparatus is a trigger generator of conventional type. In order to use Carr-Purcell method for determining relaxation time T_2, a Carr-Purcell sequence generator has been constructed. This is based on the principle of running an one-shot multivibrator with arrangement for a proper positive triggering feed-back through a feed-back amplifier. The total delay is, however, distributed over two such multivibrators in series which also makes it possible to arrange such that the multivibrators return to their initial conditions each time before being triggered. The sequence can be stopped by closing down the feed-back loop by another pulse synchronized with the repitition period generator. This is a very simple method of getting such pulse sequence with fairly good stability of pulse separations. The stability of the multivibrators can be easily improved by increasing the value of the grid-resistor (returning to high tension) in comparison to the plate-load. The circuit for Carr-Purcell sequence generator is shown in Fig. 1.

IV. EXPERIMENTAL PROCEDURE AND RESULTS

(a) *Measurement of Molecular Self-diffusion Co-efficient D :*

For the measurement of D, we observe the amplitude of the "image echo" which is formed at time, $t = 2(\tau_2-\tau_1)$ with a 90°—180°—180° pulse sequence, and as seen from the expressions in Table II, the relaxation damping of the echo-amplitude will not change with variation of τ_1, if $(\tau_2-\tau_1)$ is kept constant, whereas the diffusion damping will change. Thus we can isolate the diffusion damping from that due to relaxation. The diffusion damping of this echo can be displayed on the oscilloscope screen by triggering the sweep with a trigger-pulse which changes its

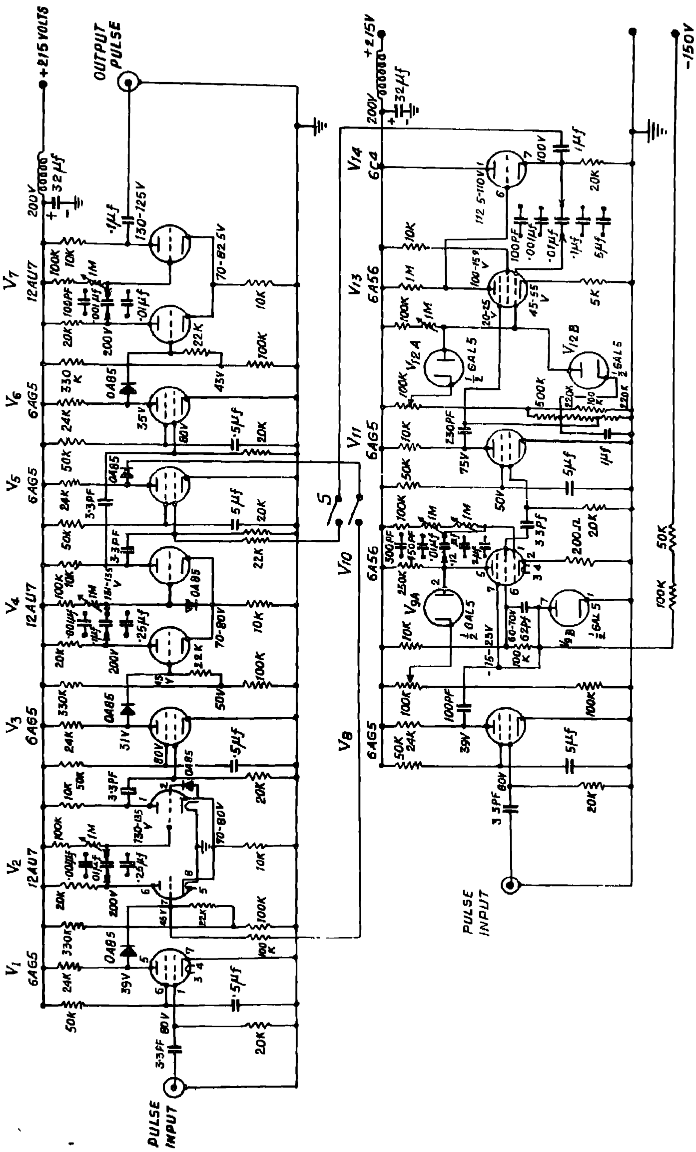

Fig. 1.—Circuit diagram of the Carr-Purcell sequence generator.

position on the time-scale as the value of τ_1, is varied. In practice, the sweep was triggered just before the third pulse by introducing a fixed delay between the second pulse and the triggering pulse. Hence as τ_1 was changed keeping $(\tau_2-\tau_1)$ constant, the triggering pulse also correspondingly changed its position, the small delay between the triggering and the third pulse, however, always remained the same. One can now obtain a multiple exposure of this echo with variation of τ_1. With the above arrangement, where the position of the image-echo is kept constant (by keeping $(\tau_2-\tau_1)$ constant), and the position of the triggering pulse is shifted exactly by the same amount as the variation in τ_1, we get a plot of the echo-amplitude *vs.* θ $[= 2(\tau_2-\tau_1) - \tau_2 = \tau_2-2\tau_1]$, θ denoting the time measured from the 3rd pulse. The triggering of the sweep was done by a pulse from a trigger-generator which is itself triggered by the second pulse such that the delay between the second and the triggering pulse can be kept constant. Fig. 2 shows such a multiple exposure.

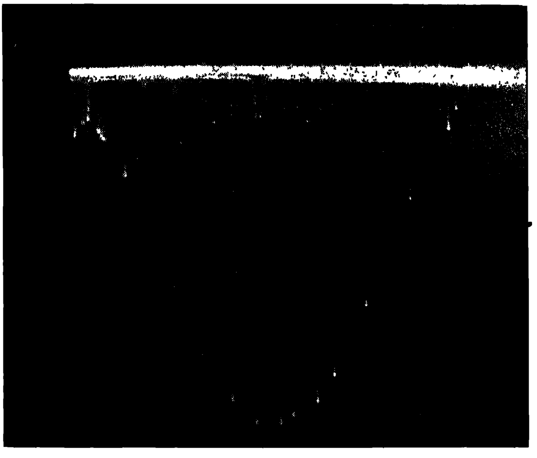

Fig. 2.—Multiple exposure of the image echo from protons in water, with variation of τ_1, keeping $(\tau_2-\tau_1)$ constant. A sequence of three pulses (90°-180°-180°) applied at times $t=0$, τ_1 and τ_2 respectively has been used. The sweep calibration with 2ms marker can be seen below the base-line.

The use of 90°—180°—180° pulse sequence with exact values of these angles is not critical, but the angle adjustments are done as accurately as possible in order to minimise the amplitudes of all other echoes which may interfere on the multiple-exposure photograph. A preliminary check is made to see that the resonance condition is reached (Ghose *et al.*, 1957*a*), the maintenance of the resonance condition being also not essential. It is, however, essential to maintain the magnetic field H_0 at a constant value. This was done in our case with the help of a flourine signal, obtained by steady NMR method

As seen in Table II, the plot of $\log_e A$ *vs* $\theta (= \tau_2 - 2\tau_1)$ where A is the echo-amplitude, is a parabola satisfying the equation

$$\log_e A = \text{constant} + 2k\tau^2\theta - 2k\tau\theta^2 \qquad (14)$$

where $\tau = \tau_2 - \tau_1 =$ constant. Thus k can be obtained from the experimental data fitting them to an equation of parabola by the standard method (Johnson, 1952) and comparing the latter with relation (14). Such a parabola is shown in the Fig. 3, k can also be evaluated from the gradients of (14) at $\theta = 0$ and $\theta = \tau$, since

$$\left[\frac{d}{d\theta}\log_e A\right]_{\theta=0} = -\left[\frac{d}{d\theta}\log_e A\right]_{\theta=\tau} = 2k\tau^2 \qquad \ldots \quad (15)$$

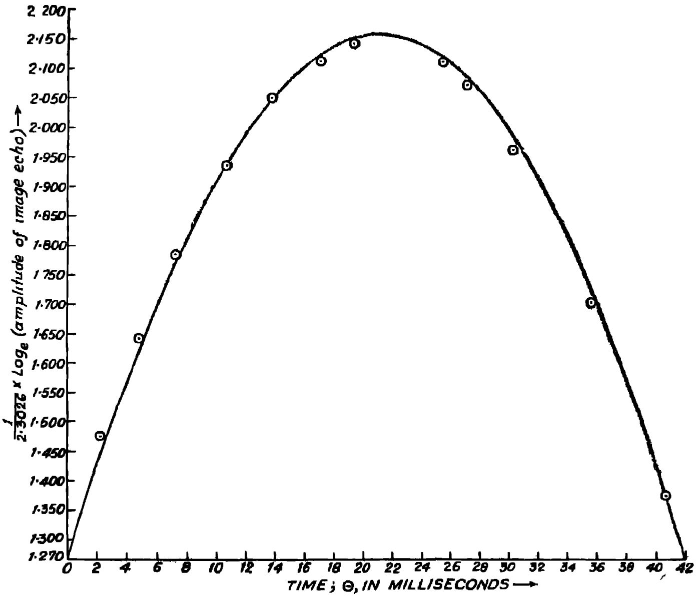

Fig. 3. The logarithm of the amplitudes of the image echo is plotted against θ, given by $\theta = \tau_2 - 2\tau_1$, where τ_1 and τ_2 give the position of the second and the third pulse respectively. The parabola fitting the experimental points are also shown (in solid line).

From the geometry of the parabola, this gradient can be evaluated simply from the relation

$$\left[\frac{d}{d\theta}\log_e A\right]_{\theta=0} = \frac{2\{(\log_e A)_{\theta=\tau/2} - (\log_e A)_{\theta=0}\}}{\tau/2} \qquad \ldots \quad (16)$$

Combining (15) and (16)

$$k = \frac{2\{(\log_e A)_{\theta=\tau/2} - (\log_e A)_{\theta=0}\}}{\tau^3} \qquad \ldots \quad (17)$$

To obtain D from the value of k, the magnitude of the magnetic field gradient, G, is required. The magnetic field gradient was applied as was suggested by Carr and Purcell by two co-axial coils of 170 turns each wound on a perspex form, the common axis of the coils being in the direction of H_0. The value of G was experimentally determined from the echo modulation. By considering in some cases six or seven such maxima or minima it was found that the maximum deviation from the average value of G as determined from the different maxima or minima was 3 to 4% at most, which indicates that the over-all field gradient along the axis of the sample holder was negligible.

The *rf* field H_1 used was approximately 5 gauss, and the proton resonance was observed at about 14 mc/sec.

D was measured with three different field gradients, 1.19, 1.71 and 2.18 gauss/cm, and was found to be the same within experimental error, the average

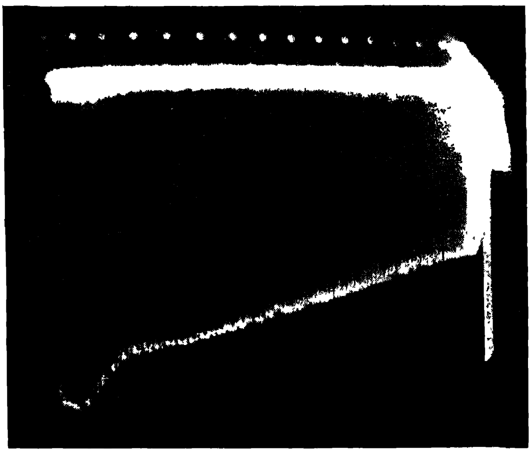

Fig. 4.—Carr-Purcell echoes from protons in water, with the magnetic field gradient 1.71 gauss/cm, almost from the beginning of the sequence. The value of τ, the separation between the first 90° and the next 180° pulses, used was 3.3 ms. Sweep calibrator marker separation was 40 ms.

value being 2.6×10^{-5}cm^2/sec for water at room temperature (30°C). The sample was doubly distilled water sealed in a pyrex glass-tube. The value of D thus determined agrees well with other measurements [Carr and Purcell (1954), Orr and Bulter (1935), Wang *et al.* (1953)]

(*b*) *Measurement of* T_2 ·

If k is known the value of T_2 can be determined in principle by Hahn's method, where the two pulse echo amplitude is corrected for diffusion damping and plotted against τ_1, the slope of the resulting straight line giving $1/T_2$. In case of protons in water the value of T_2 is comparatively large, and thus the slope will be small. Thus in this case time considered should be made large But it was found that for large values of time, the corrected echo-amplitudes do not fall on a straight line, the expected straight line showing oscillatory tendencies (giving maxima and minima with increase of time). The origin and the nature of this phenomenon is being investigated in greater details.

T_2 can, however, be determined accurately from Carr-Purcell decay constant after correcting it for diffusion damping Even for large field gradient, this correction gives good result for the value of T_2 Fig 4 shows a photograph of Carr Purcell sequence of echoes for water, the magnetic field gradient used was 1.71

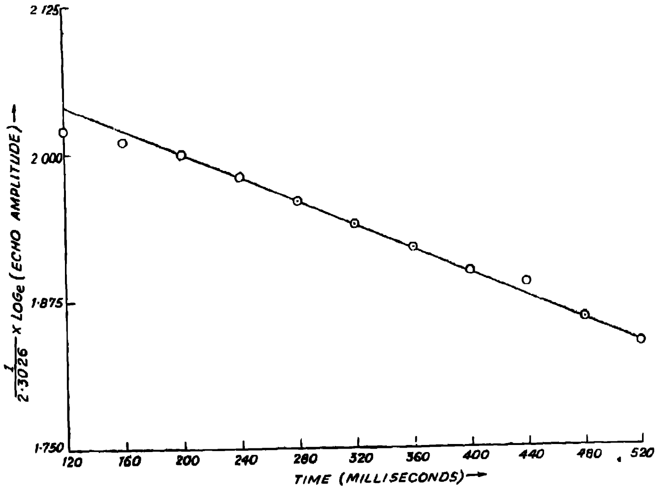

Fig. 5.—The logarithms of the echo amplitudes obtained from the Carr-Purcell sequence (Fig. 4) are plotted against time. The slope of the straight line gives $\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{3} k\tau^2$ where $k = \gamma^2 G^2 D$ and τ is the separation between the first 90° and the next 180° pulses From this, T_2 can be obtained, if k and τ are determined separately.

gauss/cm In Fig. 5 the logarithms of the echo-amplitudes are plotted against time The value of the envelope decay constant, T_2^* as obtained from Fig. 5, which is related to T_2 by the following relation

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{3}k\tau^2 \qquad \ldots \quad (18)$$

where τ is the separation between the 1st 90° pulse and the next 180° pulse, is found to be 1.99 seconds. Using the previously determined value of k and τ, the value of T_2 comes out as 2.5 seconds.

With the same sample of water, T_1 also was determined by null method (Ghose *et al.*, 1957b), and was found to be 2.88 seconds, thus the ratio of T_1/T_2 agrees well with BPP theory (Bloembergen *et al*., 1948).

In the above determinations the error creeps in mainly because of the following causes

(1) Very high degree of stability in the delays introduced by the multivibrators, in our pulsing system, cannot be expected, because of inherent instability of such systems

(2) The accuracy in time measurement is also limited as we had to calibrate the oscilloscope sweep by an external marker (Hewlett Packward, Model 100D and 202A). Even with very stable marker the time-measurement will not be correspondingly accurate since one has to measure time from the calibration of the oscilloscope sweep.

(3) The noise-figure of the apparatus limits the accuracy of measurement of the signal amplitudes and the error due to this cause is difficult to estimate exactly.

The use of scalar-type pulsing arrangement with stable oscillators as time-generators will remove the causes (1) and (2) to a large extent, and thus will improve the accuracy of measurement.

It is, however, expected that the maximum error in all our determinations was less than 5%.

(c) *Experimental check of the different theoretical approaches*

So far, the value of D, as obtained using the different theoretical formulations, was considered as a check of the theoretical approaches. This is, however, indirect. The "image" echo considered in the present work affords a direct check since the nature of variation of its amplitude with θ, is predicted to be different in different approaches. According to Hahn's approach the amplitude of this echo should not change at all. This approach is then obviously not correct, which was modified later by Herzog and Hahn*. According to Das and Saha's treatment the amplitude of this echo follows the following equation

$$\log_e A = \text{constant} + 4k\tau^2\theta - 5k\tau\theta^2 + k\theta^3 \qquad \ldots \quad (19)$$

* However, their results for liquids are not considered here for reasons explained in Section II.

and the maximum of $\log_e A$ will occur at

$$\theta = 0.465(\tau_2 - \tau_1)$$

According to the present approach, the above maximum will be at

$$\theta = 0.5(\tau_2 - \tau_1)$$

There is thus about 7% difference in the predicted positions of the maximum Experimental results on the determination of the position of this maximum favour the conclusion of the present paper. In Fig. 6 Eqns. (14) and (19) are plotted in a scale such that they are closest to each other The experimental points are then reduced to the same scale to observe which of the two curves they follow. It is found that they follow the Eq. (14) more closely than the Eq (19) showing that the present approach is more acceptable.

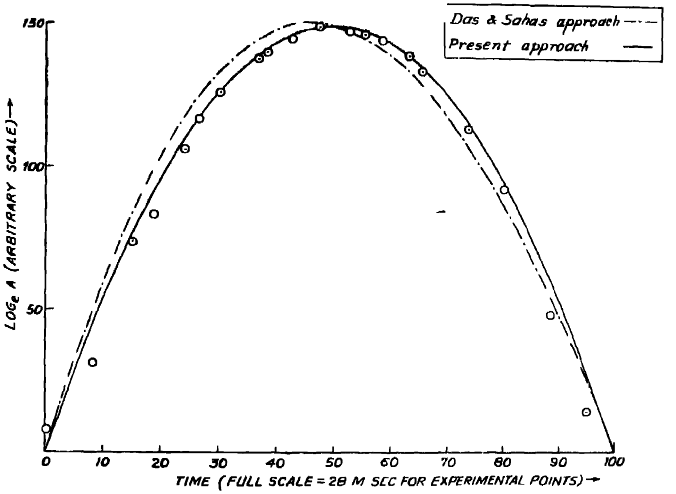

Fig. 6.—The theoretical Eqns. (14) and (19), giving the logarithms of the amplitude of the image echo, as derived from Das and Saha's and from the present treatment are drawn in the same scale for comparison with the experimental data, which are also plotted here in the same scale. The Eqns. (14) and (19) are brought to the same scale by coinciding any two points of the two curves. The two corresponding experimental points are then brought to those common points for reducing the experimental points to the common scale of the two curves.

V. DISCUSSION

Let us now examine the various different NMR methods for the measurement of D and T_2. Of all such methods*, those developed by Hahn and by Carr and Purcell are mostly used

Hahn's method of measurement of T_2 is seriously handicapped in most cases where the liquids have comparatively small viscosity. In these cases even in most homogeneous magnets ordinarily available, the diffusion effect will seriously interfere with the measurement of T_2.

Carr-Purcell's method removes this difficulty by minimizing the diffusion-effect, for which one has to use a large number of 180° rf-pulses. If the adjustment of the angles of the 180° rf-pulses is not exact, the error produces a cumulative effect and the amplitude of the echo formed after a large number of pulses becomes seriously affected. It can, however, be shown that if the echoes after a large number of pulses are considered the above effect introduces an extra damping such that the total damping remains still exponential. This extra damping can be made negligibly small if the error in the adjustment of the angle of the 180° -pulses is kept within 1-2%. This can be easily obtained One should, however, note that Meiboom and Gill (1958), have suggested a method by which the above cumulative error can be reduced. But in general case, the overall field inhomogeneity and the values of relaxation time T_2 may prevent the use of a large number of rf-pulses, which thus limits the application of the method in such cases. One can, however, adjust the field gradient such that the exponential decay of the Carr-Purcell echo sequence contains only the diffusion and the relaxation damping, the relaxation time can then be accurately determined from that decay constant, if the diffusion damping at the field gradient is ascertained independently. This is exactly what is done in the present method as described in Section IV.

We also note that while determining D from Hahn's plot (after finding out T_2 previously) Carr and Purcell found that with large field gradients there is departure from the expected straight line. This effect also limits the use of Carr-Purcell method for measuring D in general cases. Similar departure from the straight line was also observed when we attempted to evaluate T_2 from Hahn's plot, after finding out $k(=\gamma^2 G^2 D)$ previously. As mentioned earlier in Section IV, we obtained a curve showing maxima and minima, instead of a straight line This effect shows itself at large time t and increases with the increase in the value of the field gradient. Both the Carr-Purcell and the Douglas-McCall methods of measuring D from Hahn's plot will be seriously affected by the above phenomenon. In the present method this effect can be made very small even for large magnetic

* A brief account and the references of different methods of measuring T_2 can be found in "Nuclear Magnetic Resonance" by E. R. Andrew, Cambridge University Press, London (1955).

field gradient by properly adjusting the separation between the second and the third pulses, such that diffusion-damping becomes predominent in comparison with the above effect.

Though the effect of chemical shift and J-coupling (Hahn and Maxwell, 1952) will affect the amplitude of the image echo, their effect can be minimized in the present method by properly choosing the value of the magnetic field gradient. It may be mentioned here that the previous determination of D can be profitably used in the evaluation of J by the spin-echo technique (Hahn and Maxwell, 1952 and Crawford and Foster, 1956)]

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